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Dated 8 October 2003

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1/77

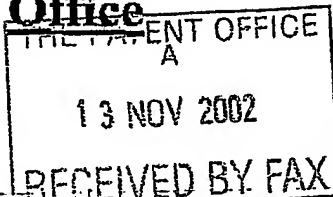
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The
 Patent
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13NOV02 E763161-1 C60121
 P01/7700 0.00-0226448.9

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
 Newport
 Gwent NP23 5TB

1. Your reference

2002CH010

2. Patent application number

(The Patent Office will fill in this part)

13 NOV 2002

0226448.9

3. Full name, address and postcode of the or of each applicant (underline all surnames)

CLARIANT INTERNATIONAL LTD

Rothausstrasse 61
 CH-4132 Muttenz

Patents ADP number (if you know it)

06971634001

If the applicant is a corporate body, give the country/state of its incorporation

Switzerland

4. Title of the invention

ORGANIC COMPOUNDS

5. Name of your agent (if you have one)

CLARIANT UK LTD

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Attn. Ms. Anne Plowden
 Calverley Lane
 Horsforth/Leeds, LS18 4RP

Patents ADP number (if you know it)

7156086001

07156086002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
 (if you know it)

Date of filing
 (day / month / year)

7. If this application is divided or otherwise derived from a earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
 (day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer "Yes" if:

Yes

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body, See note (d)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description	15 /
Claim(s)	1 /
Abstract	1 / DMC
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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Clariant International Ltd Date November 13, 2002

Dr. Dieter Dünwald

Patent Attorney

C. Hausler

Christel Heusler
Patent Administrator

12. Name and daytime telephone number of person to contact in the United Kingdom

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PATENTS FORM 1/77

ORGANIC COMPOUNDS

The invention relates to novel dyestuff and mixtures thereof, the use of such compounds
5 and/or mixtures for printing recording materials, especially paper or papery substrates,
textile fibre materials, plastic films and plastic transparencies by the inkjet printing
process and also to the recording materials printed thereby.

10 Inkjet printing processes are becoming more and more important for industrial
applications.

Inkjet printing processes are known. In what follows, the principle of inkjet printing will
only be discussed very briefly. Details of this technology are described for example in
the Ink-Jet-Printing section of R.W. Kenyon in "Chemistry and Technology of Printing
15 and Imaging Systems", Peter Gregory (editor), Blackie Academic & Professional,
Chapmann & Hall 1996, pages 113-138, and references cited therein.

In the inkjet printing process, individual droplets of the ink are sprayed from a nozzle
onto a substrate in a controlled manner. The continuous inkjet method and the drop-on-
20 demand method are employed predominantly for this purpose. In the case of the
continuous inkjet method, the droplets are produced continuously and droplets not
needed for printing are diverted into a collecting vessel and recycled. In the case of the
discontinuous drop-on-demand method, by contrast, droplets are generated and printed
as desired, i.e. droplets are only generated when this is necessary for printing. The
25 droplets may be generated for example by means of a piezo inkjet head or by means of
thermal energy (bubble jet).

By additionally disposing at least one nozzle with yellow, magenta or cyan ink side by
side it is possible to obtain colour reproductions in high quality. This process is known
30 as polychromatic printing or, when three colour components are used, as trichromatic
printing.

The composition of the invention can be used with all known and suitable inkjet printers for printing paper or papery substrates, textile fibre materials, plastic films and plastic transparencies. This applies not only to the use in monochromatic printing but also to polychromatic printing, especially trichromatic printing.

5

The composition of the ink for the inkjet printing process has to possess a suitable conductivity, sterility in storage, viscosity and surface tension to meet the specific requirements of inkjet ink. In addition, the prints on the recording materials have to have good properties and fastness.

10

Useful recording materials, as mentioned above, are preferably paper and papery substrates, textile fibre materials, plastic films and plastic transparencies. But glass and metal may be used as well.

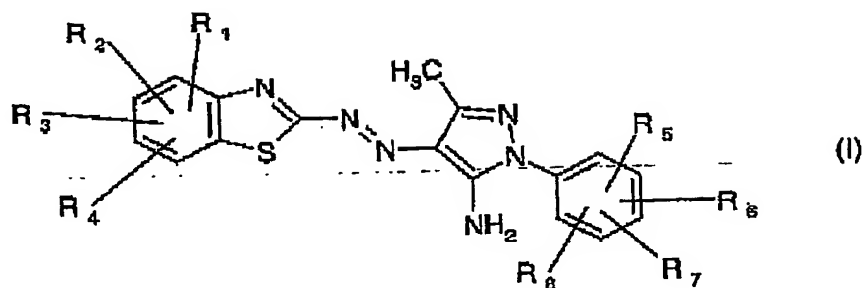
15 Useful papers or papery substrates include all known such materials. Preference is given to papers or papery substrates coated on at least one side with a material which is particularly receptive to ink compositions. Such papers or papery materials are described inter alia in DE 3018342, DE 4446551, EP 164196 and EP 875393.

20 Useful textile fibre materials are in particular hydroxyl-containing fibre materials. Preference is given to cellulosic fibre materials, which consist of or comprise cellulose. Examples are natural fibre materials such as cotton, linen or hemp and regenerated fibre materials such as, for example, viscose and also lyocell.

25 Useful plastic films or plastic transparencies include all known such materials. Preference is given to plastic films or plastic transparencies coated on at least one side with a material which is particularly receptive to the ink compositions. Such plastic films or plastic transparencies are described inter alia in EP 755332, US 4935307, US 4956230, US 5134198 and US 5219928.

30

This invention provides dyestuff according to the formula (I)



wherein

R_1, R_2, R_3, R_4 , independently from each other signifies H, SO_3H , SO_2R , $\text{SO}_2\text{NR}'\text{R}''$,
5 COOR , COOH , OH , alkoxy, NCOCH_3 , or $\text{NR}'\text{R}''$, or two of the substituents R_1, R_2, R_3 ,
or R_4 form together a ring which is annealed to the benzthiazole moiety

R_5, R_6, R_7, R_8 , independently from each other signifies H, Methoxy, Alkyl, Aryl,
Alkoxy, SO_3H , SO_3R , Cl, Br, F, NRR'' , $\text{SO}_2\text{-CH}_2\text{-CH}_2\text{-OH}$, or or two of the substituents
10 R_5, R_6, R_7 , or R_8 , form together a ring which is annealed to the phenyl group of the
aminopyrazolo moiety.

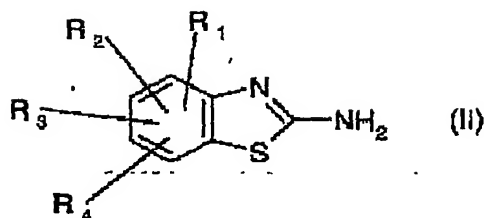
R, R' and R'' are independently from each other H, alkyl or alkoxy or arylgroups
groups.

15

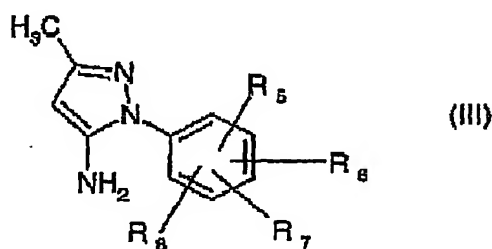
Alkyl and alkoxy groups referred to above are preferably radicals

Alkyl and alkoxy groups referred to above are preferably radicals with up to 8 carbon
atoms, more preferably up to 4 carbon atoms, e.g., butyl and more preferably 1 or 2
20 carbon atoms; any substituents thereon may be halogen, hydroxy, cyano, alkoxy, acyl,
acyloxy or acylamino. Those alkyl or alkoxy groups having 3 or more carbon atoms
may be straight-chain, branched or cyclic, for example, cyclohexyl.

25 The invention provides in another of its aspects a process for the production of the
dyestuffs according to the formula I wherein a diazotised amine of formula II



is coupled with a compound of formula III;



5

The compounds of formulae II and III are known starting materials, although they may also be readily synthesised from commonly available reagents via known syntheses. Diazotisation and coupling are effected in the usual manner. Preferably the amine II is diazotised at a temperature of from 0 DEG to 20 DEG C. and at a pH of from 0 to 2, more preferably 0 to 1. The coupling reaction is preferably carried out at a temperature of from 0 DEG to 40 DEG C. and at a pH of from 0 to 7, more preferably 0 to 4.

Dyestuffs according to the formula (I) may be isolated from the reaction medium according to known methods, for example, by salting out with an alkali metal salt, filtering and drying optionally in vacuo at a slightly elevated temperature.

Depending upon the reaction and/or isolation conditions, the dyestuffs according to the formula (I) may be obtained as the free-acid, salt or mixed salt form, containing, for example, one or more cations selected from the alkali metal cations, e.g., the sodium ion, or an ammonium ion or an alkylammonium cation, e.g., mono-, di-, or tri-methyl or ethylammonium cations. The dyestuffs may be converted from the free-acid form to a salt or mixed salt form or vice-versa or from one salt form to another according to conventional techniques.

25

The compounds of formula (I) may be converted into dyeing preparations. Processing into stable liquid, preferably aqueous, or solid (granulated or powder form) dyeing preparations may take place in a generally known manner.

A further embodiment of the invention relates to the use of the above mentioned compositions for the ink-jet printing process.

In the following examples, the temperatures are given in degrees celsius. The percentages and parts are understood to be by weight.

EXAMPLE

173g of methanilic acid were diazotized at 0 to 5 °C and reduced by 269g Sodium sulfite in the presence of 40 sodium hydrogencarbonate at 14 to 16°C. after this step the product was hydrolized by adding 330g sulfuric acid (85%) at 75°C. The resulting hydrazine was filtered off and at pH 7 reacted with 82g 3-Aminocrotonic nitrile. The product was presipitated by adding 350g hydrochloric acid, filtered off, washed and dried which yields a press cake of 270g of 1-(3'-sulfophenyl)-3-methyl-5-aminopyrazol.

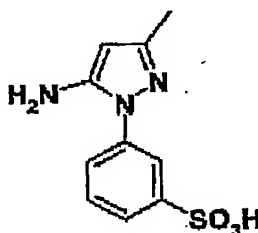
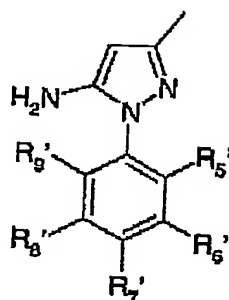

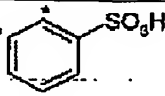
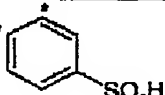
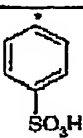
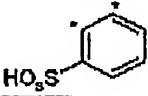
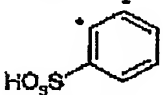
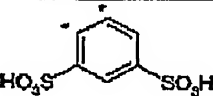


Table 1: substituted aminopyrazoles



5

Code	R ₅ '	R ₆ '	R ₇ '	R ₈ '	R ₉ '
1	SO ₃ H	-	-	-	-
2	CH ₃	-	SO ₃ H	-	-
3	SO ₃ H	-	-	SO ₃ H	-
4	-	SO ₃ H	-	-	-
5	-	SO ₃ H	NH ₂	-	-
6	-	SO ₃ H	OCH ₃	-	-
7	-	CH ₃	SO ₃ H	-	-
8	-	NH ₂	SO ₃ H	-	-
9	-		-	-	-
10	-	-	SO ₃ H	-	-
11	-	-	COOH	-	-
12	-	-		-	-
13		-	SO ₃ H	-	-

14	SO ₃ H		-	-
15	-		-	-
16	-		-	-
17	-		-	-
18	-		-	-
19	SO ₃ H		-	-
20	-		-	-

5 EXAMPLE

218g 2-amino-nitrobenzene-5-sulfonic acid were added to 1100ml of a 1.0 Molar Sulfuric acid at 5°C and diazotized. The resulting suspension was slowly added a solution of 180ml water, 152g NH₄SCN and 5g Cu(SCN)₂ at 0 to 5 °C and stirred for additional 3 hours at room temperature. The reaction mixture was poured into a hot (90 to 95°C) suspension of 1000ml water, 500g iron powder and 17g of a 37% hydrochloric acid and the resulting suspension was stirred till the reduction was completed. The mixture was brought to a pH of more than 9 and the iron slurry was filtered off. The product was precipitated by lowering the pH, filtered off, washed and dried. this yields 200g product (2-Amino-benzthiazole-5-sulfonic acid) as a press cake.

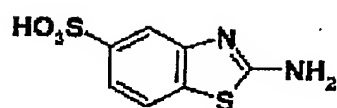
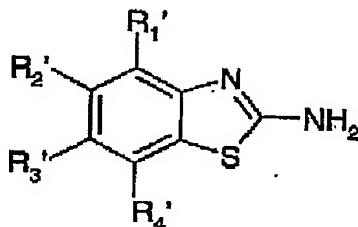
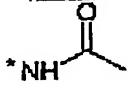

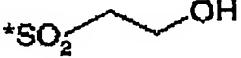
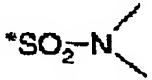
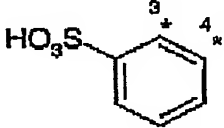


Table 2: substituted benzthiazoles:

5

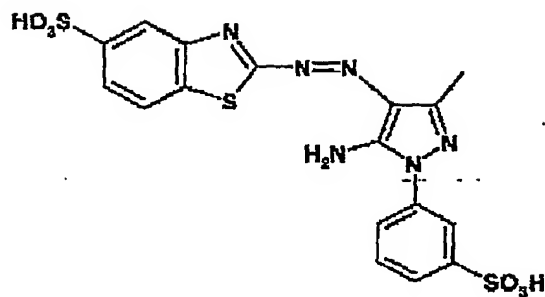


Code	R ₁ '	R ₂ '	R ₃ '	R ₄ '
1	SO ₃ H	-	-	-
2	SO ₃ H	-	CH ₃	-
3	SO ₃ H	-	OCH ₃	-
4	COOH	-	-	-
5	OCH ₃	-	-	-
6	-	OCH ₃	-	-
7	-	SO ₃ H	-	-
8	-	SO ₃ H	OCH ₃	-
9	-	SO ₂ NH ₂	-	-
10	-	-	SO ₃ H	-
11	-	-	COOH	-
12	-	-	COOCH ₃	-
13	-	-	COOEt	-

14	-	-	NH ₂	-
15	-	-		-
16	-	-	OCH ₃	SO ₃ H
17	-	-		-
18	-	-		-
19	-	-		-
20	-	-	-	COOH
21	-	-	-	SO ₃ H
22	-	-		

5 EXAMPLE

To 500g sulfuric acid (98%) 40g sodium nitrite were added and cooled to 5°C. To the cooled solution 115g 2-Amino-benzthiazole-5-sulfonic acid were added while adding 625g of crushed ice to keep the temperature low. After the diazotation of the 2-Amino-benzthiazole-5-sulfonic acid has been completed, this suspension was added to a solution of 1000ml water and 127g 1-(3'-sulfophenyl)-3-methyl-5-aminopyrazol. The pH was kept at about pH 5 to 6 by adding about 1330g of a 30% NaOH solution. The mixture was stirred until the coupling was completed. The resulting dye was purified by diafiltration

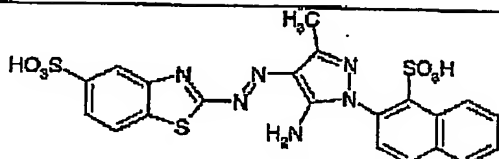
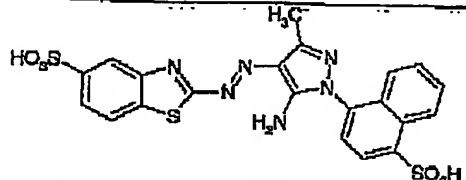
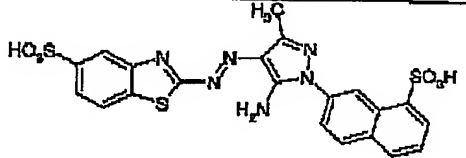
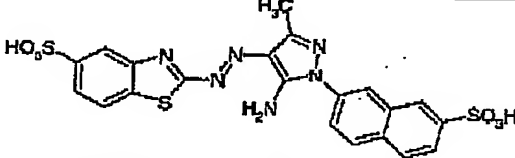
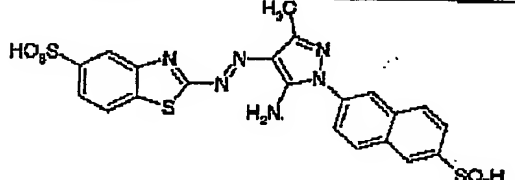
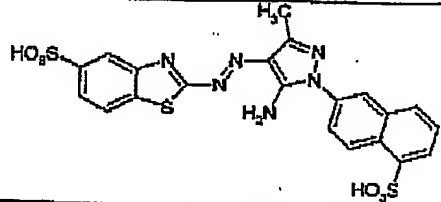
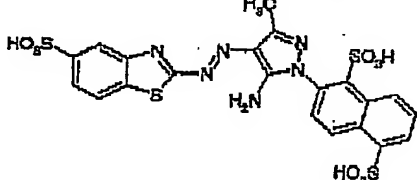
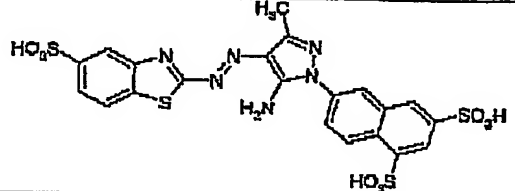


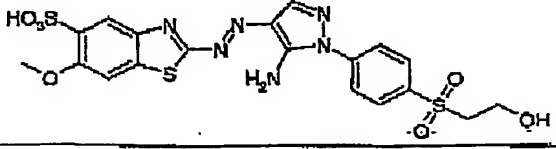
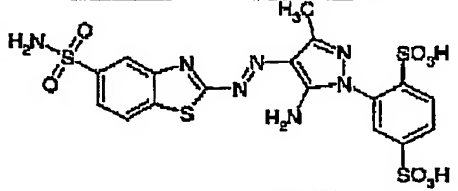
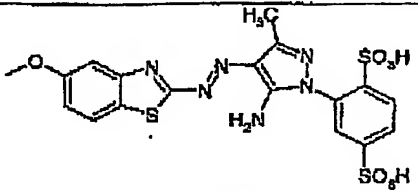
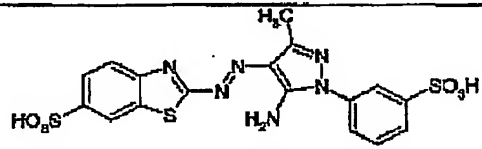
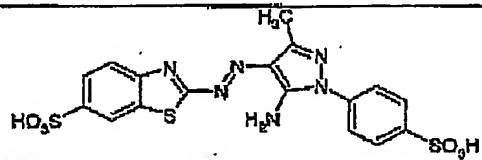
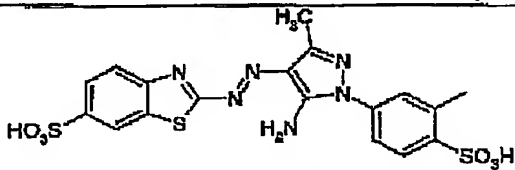
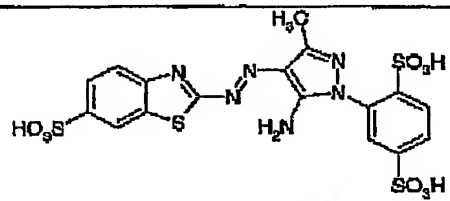
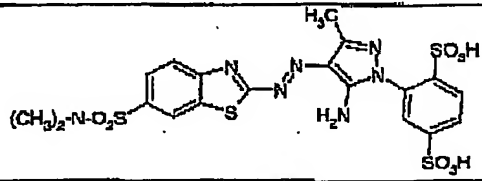
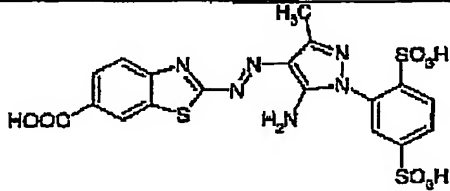
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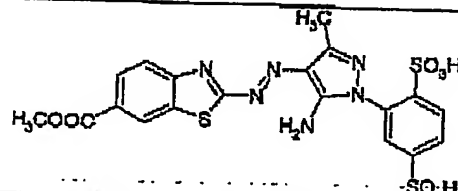
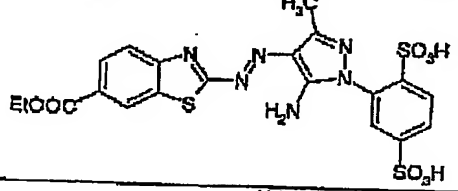
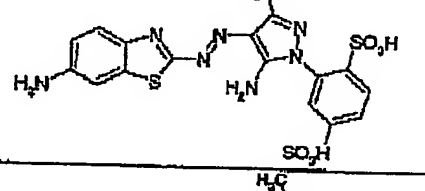
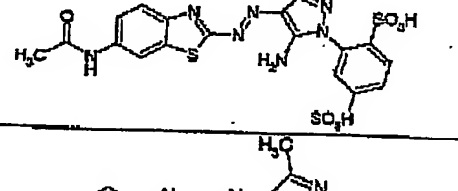
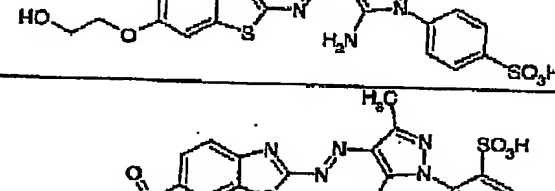
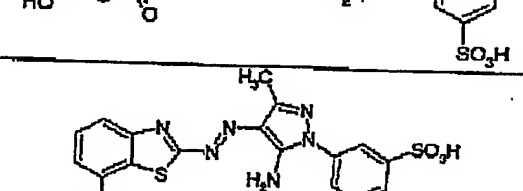
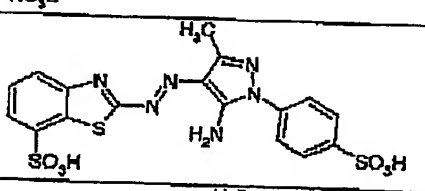
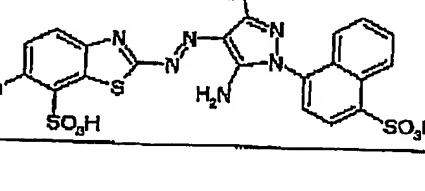

The affinity of this dyestuff was excellent (>95%). The migration of the dyestuff, which is decisive for the levelness of the dyeings, and its fastness, especially light and wet fastness, and also its boiling resistance, were very good.

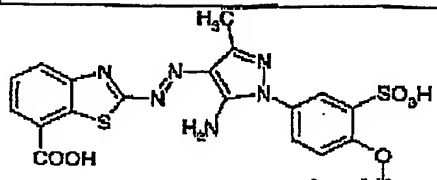
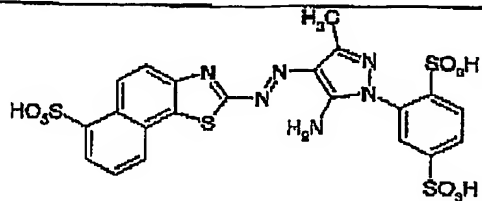
dye Nr..	Struktur	λ_{max}
1		408,3
2		404,9
3		427,4
4		435,1
5		439,7

6		453,2
7		443,0
8		449,0
9		449,2
10		448,3
11		452,1
12		452,3
13		454,2
14		452,2

15		462,1
16		462,4
17		461,7
18		463,2
19		460,3
20		461,3
21		463,8
22		468,2

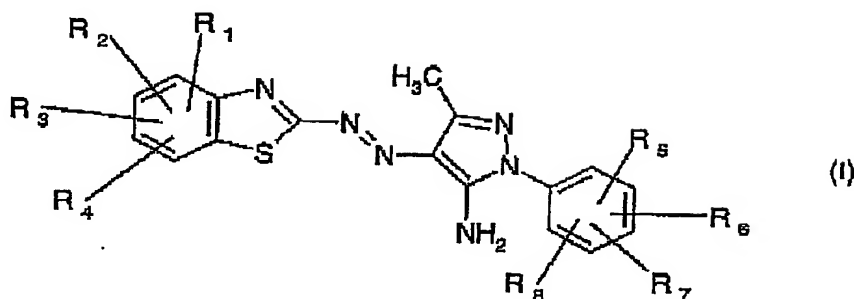
23		443,7
24		454,3
25		459,5
26		453,0
27		452,5
28		451,8
29		455,9
30		459,7
31		454,7

32		453,2
33		453,8
34		472,8
35		459,0
36		458,1
37		457,4
38		389,7
39		371,8
40		458,1

41		442,9
42		470,3

Claims

1. dyestuff according to the formula (I)



wherein

10 R_1, R_2, R_3, R_4 , independently from each other signifies H, SO_3H , SO_2R , SO_2NRR'' , $COOR$, $COOH$, OH , alkoxy, $NCOCH_3$, or $NR'R''$, or two of the substituents R_1, R_2, R_3 , or R_4 form together a ring which is annealed to the benzthiazole moiety

15 R_5, R_6, R_7, R_8 , independently from each other signifies H, Methoxy, Alkyl, Aryl, Alkoxy, SO_3H , SO_3R , Cl, Br, F, $NR'R''$, $SO_2-CH_2-CH_2-OH$, or two of the substituents R_5, R_6, R_7 , or R_8 , form together a ring which is annealed to the phenyl group of the aminopyrazolo moiety.

R, R' and R'' are independently from each other H, alkyl or alkoxy or aryl groups

20

and the salts and mixtuers thereof.

2. A process of dyeing or printing fibrous materials consisting of natural and/or synthetic polyamides by applying thereto dyestuffs according to formula I as defined in claim 1, their salts or mixtures thereof.

25

3. Fibrous materials consisting of natural and/or synthetic polyamides dyed with dyestuffs of formula (I) as defined in claim 1, their salts or mixtures thereof.

case 2002CH010

Abstract

----- The invention relates to novel azo-dyestuffs, the use of such compounds and/or mixtures-
5 for printing recording materials, especially paper or papery substrates, textile fibre
materials, plastic films and plastic transparencies by the inkjet printing process and also
to the recording materials printed thereby.

PCT Application
IB0305096



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